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(54) Title: FUEL ADDITIVES

(57) Abstract: There is described a surfactant composition comprising an alkanolamide, an alkoxyated alcohol, an alkoxyated fatty acid and a nitrogen compound, e.g. urea. There is also described a fuel composition comprising a hydrocarbon fuel and urea and also a method of running a combustion engine using the fuel of the invention.

## FUEL ADDITIVES

This invention relates to a novel fuel composition and to methods of their preparation and use.

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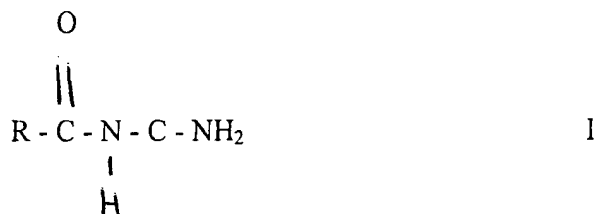
Internal combustion engines which burn hydrocarbon fuels operate at very high temperatures. These high temperatures cause the oxidation of various nitrogenous materials, including nitrogen and organic and inorganic nitrogen compounds, to nitrogen oxides. Various nitrogenous oxides (NO<sub>x</sub>) can be produced, such as nitric  
 10 oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitrogen trioxide (NO<sub>3</sub>), dinitrogen trioxide (N<sub>2</sub>O<sub>3</sub>), tetranitrogen pentoxide (N<sub>4</sub>O<sub>5</sub>), nitrous oxide (N<sub>2</sub>O), etc.

NO<sub>x</sub> is extremely undesirable and is implicated in respiratory disorders, such as asthma, and is present in smog and acid rain. There has therefore long been a need to  
 15 reduce NO<sub>x</sub> emissions produced during the combustion of fossil fuels.

Ureas are known to be useful in the reduction of NO<sub>x</sub> and they have been known to be used in, for example, power stations. However, thus far, their utility in the combustion of liquid hydrocarbon fuels such as gasoline, diesel or aviation fuel, has  
 20 been very limited due to urea's sparing solubility in such fuels.

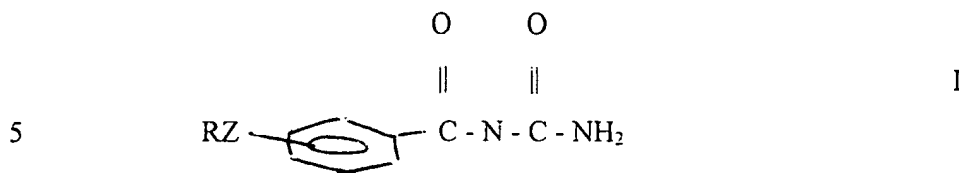
United States Patent No. 5,292,351, De Rosa, et al, attempts to overcome this problem by the use of mixture of ureas, generally a mixture of an alloyl urea of formula I,

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and an aroyl urea of formula II,



However, the compositions are expensive to manufacture which contrasts with the use of urea which is available cheaply as a bulk chemical.

10 International Patent Application No. WO99/35215, Wenzel, describes an additive for combustible fuels which includes a nitrogen source, such as urea. Whilst the additive is said to reduce NO<sub>x</sub>, the compositions are very complex and include numerous ingredients, including:

- a water soluble alcohol,
- 15 a C6 to C12 alcohol,
- a C6 to C18 ethoxylated alcohol,
- a C10 to C24 fatty acid, and
- a nitrogen source.

20 Moreover, significantly high amounts of additive need to be present to achieve an effective result. Although in one or two of the examples the ratio of fuel:additive may be as high as 95:5, it is generally considered to be in the range of 60:40 or 85:15. Since such additives are expensive to manufacture the cost of using additives such as this is prohibitive. Also, the amount of nitrogen base which can be incorporated in a

25 fuel is severely restricted by the requirement that it is stoichiometrically less than the fatty acid used in the formulation since the specification clearly states that the fatty acid is only partially neutralised by the nitrogen base. It is also notable that the fuel compositions exemplified in the prior art of Wenzel all have significant amounts of water present which will aid in the solubilisation of nitrogen compounds, such as

30 urea.

International Patent Application No WO 98/17745 describes an alternative formulation which comprises,

- 25% w/w of a diethanolamide,
- 50% w/w of an ethoxylated alcohol, and
- 5 25% w/w of a fourteen carbon chain fatty acid with seven ethoxylate groups.

WO '745 especially describes fuel compositions comprising, *inter alia*, an additive made up of a fatty acid diethanolamide, an alcohol ethoxylate and an ethoxylate of a fatty acid, the degree of ethoxylation being selected so that a long term stable fuel  
10 composition is formed and, in particular, wherein, by carefully selecting the degree of ethoxylation, a balanced blend can be produced.

Whilst such additives provide significant reductions in emissions and are useable at low concentrations, there is still a need for a fuel composition which is capable of  
15 reducing emissions whilst maintaining performance levels.

We have now surprisingly found that the additives described by Williamson et al are suitable for use in very low fuel:additive ratios in combination with nitrogenous compounds such as urea.

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Thus according to the invention we provide a surfactant composition comprising an alkanolamide, an alkoxylated alcohol, an alkoxylated fatty acid and a nitrogen compound.

25 The alkanolamide is preferably an ethanolamide and more preferably a diethanolamide. Especially preferred are the diethanolamides and particularly the super diethanolamides. By the term super diethanolamide we mean a diethanolamide in which the nitrogen is substituted by an acyl substituent e.g. acyl C5 to C18, preferably C8 to C18, more preferably C10 to C18 and especially C18, oleic  
30 diethanolamide. Where the amides are derived from natural products this moiety will

have an even number of carbon atoms, e.g. 18 for the oleyl derivative. Note, the alkyl part of this group is the R group which will be an odd number.

There are three commercial routes to alkanolamides;

- 5        Acid + alkanolamine = alkanolamide + water  
         Plant or animal oil (triglyceride) + alkanolamine = alkanolamide+glycerol  
         Methyl ester + alkanolamine = alkanolamide + methanol

- 10       These are listed in order of increasing product quality. The route via the acid often uses an excess of alkanolamine to produce a product higher in amide than is obtainable from the acid if a stoichiometric ratio is used; these products are sometimes referred to as super amides.

- 15       The alkoxyated alcohol is preferably an ethoxylated alcohol. It is essential that the ethoxylated alcohol is an oil soluble alcohol. Therefore, alkanols are preferred and these may be primary, secondary or tertiary alkanols and especially primary alkanols. As the oil solubility of the alcohol may vary with the carbon chain length of the ethoxylated alkanol, the alkanol is preferably a C5 to C22 alkanol, more preferably C5 to C15 alkanol. The ethoxylated alcohol may comprise a mixture of alkanols.  
20       However, it is preferred that in such mixtures one alkanol will predominate. Thus, the most preferred alkanol is predominantly a C9 to C11 alkanol. In addition the degree of ethoxylation of the alcohol may be varied and the oil solubility will, generally, decrease with the increase in the degree of ethoxylation. It is preferred that the ethoxylate to alcohol ratio is greater than 2. More preferably, the ethoxylate to  
25       alcohol ratio is from between 1 and 10, preferably between 1 and 5, more preferably between 1 and 3 and especially between 2 and 3. A commercially available ethoxylated alcohol is especially preferred in which the ethoxylate to alcohol ratio is 2.75. Such an alcohol ethoxylate is available as NEODOL 91/2.5.

- 30       The fatty acid ethoxylate may comprise any conventionally known fatty acid ethoxylate. Thus the fatty acid ethoxylate may be derived from a fatty acid having

from 8 to 20 carbon atoms, preferably from 10 to 18 and most preferably 18 carbon atoms (oleic acid).

5 The degree of ethoxylation is chosen to optimise performance in the blend with the other two selected surfactants and may be from 1 to 20, but more preferably from 5 to 12. A suitable product within this range would be, for example that derived from the addition of 7 molecules of ethylene oxide to 1 mole of oleic acid.

10 The preferred additive of this invention is a non-ionic surfactant and preferably a blend of surfactants. It is a preferred feature of this invention that the surfactants be selected by their nature and concentration that the additive (as well as any water or other non-fuel liquid present) be solubilised within the fuel. For this purpose it is convenient to have regard to the hydrophilic-lipophilic (HLB) of the surfactant, the value being calculated according to the expression.

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$$\text{HLB} = \frac{\text{mol. wt of hydrophilic chain} \times 20}{\text{total mol. wt.}}$$

20 The values will depend on the length of the hydrophilic chain, typically an ethoxylate chain. The length of the chain will increase the extent of solubilisation because of a greater ability to solubilise.

25 As with the compositions described in WO98/17745, a blend of surfactants is preferred, preferably by selecting one appropriate to the fuel, say 10 to 18 for hydrocarbon fuel, most preferably 13. In the case of an alcohol the HLB value of the surfactant is between 3 and 7, most preferably about 4. But the addition of surfactants normally create ratios of 1:1 or high volume emulsions or 5:1 ratios when the solubilisation is required at 1:100.

The invention has the ability to unify the HLB requirements of any liquid fuel which in turn allows for one dose to be used in any fuel from C5 carbon chains up. The benefit being the amount of treatment directly related to the co-solvency ability.

- 5 Preferably the ethoxylate of the fatty acid makes up about 25% by volume of the additive and further preferably the alcohol ethoxylate comprises 50% by volume of the additive.

- 10 An additive of the invention may be added to a hydrocarbon fuel, e.g. diesel, petrol or alcohol, such as ethanol which may or may not be contaminated with water. The invention is seen to particularly good effect when added to synthetic fuels based on low fraction oils.

- 15 The concentration of the additive can be very low, typically of the order of 0.1 - 2 % v/v, preferably 0.5 - 2 %v/v. There appears to be no technical or economic benefit in adding more unless a co-solvent dual action is required, when the priority will be dosage against performance.

- 20 The nitrogen compound may be selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl. Urea is preferred. The nitrogen compound may be an anhydrous compound or a hydrous compound, e.g. an aqueous solution.

- 25 The presence of the additive of the invention ensures that the fuel composition forms a consistent stable homogenous composition and creates a monolayer simultaneously a result of which leads to a better more complete burn which reduces pollution and increases miles per gallon.

As a result a blended fuel, particularly alcohol based, is able to combust more precisely with a cooler charge to reduce the iron-formates present from the aldehyde peracids and peroxide reactions normally attributable to engine degradation.

- 5 In a further aspect of the invention we provide a fuel composition comprising a liquid hydrocarbon fuel and a surfactant composition as hereinbefore described.

In the fuel composition of the invention the hydrocarbon fuel, may be any conventionally known fuel, e.g. gasoline, diesel, biodiesel, etc. Furthermore the fuel  
10 of the invention may, optionally, include an oxygenator. The oxygenator may be an alcohol, such as ethanol. When an oxygenator such as ethanol is present, the amount of ethanol in the fuel may vary and may be from 0 to 25% v/v ethanol, preferably from 1 to 10% v/v ethanol.

- 15 We further provide a method of running an internal combustion engine comprising the use of a fuel of the invention.

According to a yet further feature of the invention we provide a method of solubilising a nitrogen compound in a fuel composition which comprises mixing a  
20 hydrocarbon fuel, a nitrogen compound and a surfactant composition as hereinbefore described.

We also provide the use of a nitrogen compound in the manufacture of a fuel additive of the invention. We especially provide the use of urea in the manufacture of a fuel  
25 additive of the invention.

A particular advantage of the present invention over the prior art is that fuel compositions may be prepared which are substantially anhydrous, save for trace water contamination. By the term trace water contamination we generally mean 0.1  
30 %w/w water or less. This clearly contrasts with the prior art of WO99/35215 which water present to solubilise the urea in the formulation. Thus, according to a yet



further feature of the invention we provide the use of urea in the manufacture of a substantially dry fuel composition which provides reduced NOx emissions.

We also provide a method of running an engine adapted to use an alcohol-based fuel,  
5 comprising adding to the fuel a miscible additive selected to solubilise the fuel and the additive so eliminating the deposit of by-products formed during the combustion of the fuel.

The invention will now be illustrated, but in no way limited, with reference to the  
10 accompanying examples

### Example 1

A surfactant composition was made up by blending three constituents viz. C9-11  
15 alcohol ethoxylated with 2.7moles EO; the super diethanolamide of oleic acid; and ethoxylated oleic acid in the ratio 2:1:1.

1% of this composition was added to 7.7% ethanol/ 92.3%diesel blends, including  
Certification diesel, U.S No1 diesel, 10% aromatic diesel containing 0.1% cetane  
20 improver resulting in optically clear and stable micro-emulsion fuels. These were tested as automotive fuels on a 1991 Detroit Diesel Series 60 engine using the EPA(USA Environmental Protection Agency) heavy duty engine certification test as described in the Code of Federal Regulations ,Title 40, Part 86, Subpart N.

25 Toxic exhaust gas emissions were measured and compared with those of the base un-additised diesels. Significant reductions were obtained of toxic gases CO, CO2, NOx and particulate matter.

**Example 2**

A solution of 0.25% urea in ethanol was blended in a 7.7:92.3 ratio with US No1 diesel and 1.0 % of the surfactant mixture described in Example 1, was added to  
5 produce a clear micro-emulsion automotive fuel.

Tests using this blend showed that toxic gas emissions were again lower than the base fuel, the urea having made a contribution to the reductions obtained.

**10 Example 3**

A blend was made of certification diesel, biodiesel and ethanol, stabilised with the surfactant additive described in Example 1. Emission tests showed reductions in CO, NOx and particulate matter compared with base diesel.

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**CLAIMS**

1. A surfactant composition comprising an alkanolamide, an alkoxyated alcohol, an alkoxyated fatty acid and a nitrogen compound.
- 5 2. A surfactant composition according to Claim 1 characterised in that the alkanolamide is an ethanolamide
3. A surfactant composition according to Claim 3 characterised in that the alkanolamide is a diethanolamide.
- 10 4. A surfactant composition according to Claim 3 characterised in that the diethanolamides are super diethanolamides.
5. A surfactant composition according to Claim 3 characterised in that the  
15 nitrogen in the diethanolamide is substituted by an acyl C5 to C20 substituent.
6. A surfactant composition according to Claim 5 characterised in that the diethanolamide is substituted by an acyl C8 to C18 substituent.
- 20 7. A surfactant composition according to Claim 6 characterised in that the diethanolamide is substituted by an acyl C10 to C18 substituent.
8. A surfactant composition according to Claim 7 characterised in that the diethanolamide is a oleic diethanolamide.
- 25 9. A surfactant composition according to Claim 1 characterised in that the alkoxyated alcohol is an ethoxyated alcohol.
10. A surfactant composition according to Claim 9 characterised in that the  
30 ethoxyated alcohol is an oil soluble alcohol.

11. A surfactant composition according to Claim 9 characterised in that the ethoxylated alcohol is an alkanols.
- 5 12. A surfactant composition according to Claim 11 characterised in that the ethoxylated alcohol is a primary alkanols.
13. A surfactant composition according to Claim 11 characterised in that the alkanol is C5 to C22 alkanol.
- 10 14. A surfactant composition according to Claim 11 characterised in that the ethoxylated alcohol comprises a mixture of alkanols in which one alkanol predominates.
- 15 15. A surfactant composition according to Claim 11 characterised in that the predominate alkanol is a C9 to C11 alkanol.
16. A surfactant composition according to Claim 9 characterised in that the ethoxylate to alcohol ratio is from between 1 and 10.
- 20 17. A surfactant composition according to Claim 16 characterised in that the ethoxylate to alcohol ratio is from between 1 and 5.
18. A surfactant composition according to Claim 17 characterised in that the ethoxylate to alcohol ratio is from between 2 and 3.
- 25 19. A surfactant composition according to Claim 18 characterised in that the ethoxylate to alcohol ratio is 2.75.
20. A surfactant composition according to Claim 19 characterised in that the ethoxylated alcohol is NEODOL 91/2.5.
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21. A surfactant composition according to Claim 1 characterised in that the fatty acid group is a C8 to C20 fatty acid.
22. A surfactant composition according to Claim 21 characterised in that the fatty acid group is a C10 to C18 fatty acid.
23. A surfactant composition according to Claim 22 characterised in that the fatty acid group is a C18 fatty acid (oleic acid).
24. A surfactant composition according to Claim 1 characterised in that the composition comprises 25% v/v of the fatty acid.
25. A surfactant composition according to Claim 1 characterised in that the composition comprises 50% v/v of the alcohol ethoxylate.
26. A surfactant composition according to Claim 1 characterised in that the nitrogen compound is selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl.
27. A surfactant composition according to Claim 26 characterised in that the nitrogen compound is urea.
28. A fuel composition comprising a liquid hydrocarbon fuel and a surfactant composition according to claim 1.
29. A fuel composition according to claim 28 characterised in that the surfactant content is from 0.1-2.0% v/v.

30. A fuel composition according to Claim 28 characterised in that the fuel is a diesel.
- 5 31. A fuel composition according to Claim 29 characterised in that the diesel is a biodiesel.
32. A fuel composition according to Claim 28 characterised in that the fuel is a gasoline.
- 10 33. A fuel composition according to Claim 28 characterised in that the mixture also comprises an oxygenator.
34. A fuel composition according to Claim 39 characterised in that the oxygenator is an alcohol.
- 15 35. A fuel composition according to Claim 40 characterised in that the alcohol is ethanol.
- 20 36. A fuel composition according to Claim 41 characterised in that the fuel comprises from 0 to 25% v/v ethanol.
37. A fuel composition according to Claim 42 characterised in that the fuel comprises from 1 to 10% v/v ethanol.
- 25 38. A method of solubilising a nitrogen compound in a fuel composition which comprises mixing a hydrocarbon fuel, a nitrogen compound and a surfactant composition according to claim 1.
- 30 39. A method of running an internal combustion engine comprising the use of a fuel according to claim 28.

40. The use of a nitrogen compound in the manufacture of a fuel additive according to Claim 1.
41. The use of according to claim 40 characterised in that the nitrogen compound is urea.
42. The use of urea in the manufacture of a substantially dry fuel composition which provides reduced NO<sub>x</sub> emissions.
43. A fuel composition which is substantially dry a comprises a hydrocarbon fuel, urea and a surfactant additive.
44. A method of running an engine adapted to use an alcohol-based fuel, comprising adding to the fuel a miscible additive selected to solubilise the fuel and the additive so eliminating the deposit of by-products formed during the combustion of the fuel.
45. A fuel additive or a fuel composition substantially as described with reference to the accompanying examples.

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